Stimulated Heterogeneous Nucleation of Supercooled Liquid H$_2$ Droplets

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Abstract. The properties of H$_2$ droplets formed by condensation in a supersonic freejet were probed by the capture and coagulation of CO molecules for the purpose of determining whether the droplets are liquid or solid. The CO was introduced into the H$_2$ droplets by passing the droplet beam through a scattering chamber containing CO at room temperature and various pressures. Reduction of droplet size as a result of droplet collisions with CO molecules was determined by measuring the droplet size downstream from the scattering region for several different values of the CO pressure. The size of the embedded clusters formed by coagulation of the captured CO molecules was determined from the mass spectra measured for several values of CO pressure in the scattering chamber. A comparison of (a) the observed dramatic loss of about 7% of the H$_2$ molecules from a droplet after between 2 and 8 collisions with (b) the loss predicted due to evaporation/sublimation in the event of solidification is taken to be compelling evidence that the H$_2$ droplets were liquid prior to their collisions with the CO scattering gas. The observed dependence of the maximum CO cluster size on the collision frequency appears to indicate that a sufficiently high collision frequency will liquify a droplet which otherwise would be solid. This observation supports the conclusion that the H$_2$ droplets are solidified as a consequence of heterogeneous nucleation induced by the captured CO molecules. The evidence in favor of a liquid state, coupled with the estimated 4K droplet temperature, suggest strongly that the supercooled H$_2$ droplets are superfluid.

INTRODUCTION

Previous experimental studies of the properties of H$_2$ droplets formed in freejet expansions are described in earlier papers [1-3]. The objective of this series of studies is the production of metastable p-H$_2$ droplets in the liquid state with temperatures below 6K with the hope that such droplets will exhibit superfluid properties. In the first paper [1], droplet temperatures as low as 6K were deduced from measured values of terminal droplet velocities; evaporation produces additional cooling to about 4K. In the second paper [2], dramatically higher terminal droplet velocities were observed for measurements made on p-H$_2$ which apparently had been inadvertently contaminated in the source with some foreign substance; it was conjectured that this foreign substance provided sites for heterogeneous nucleation of solid p-H$_2$ during the expansion and that the heat released in solidification was converted into additional terminal velocity. In the study described here, evidence that the H$_2$ droplets are liquid was sought by deliberately arranging for the capture of a foreign substance, in this case CO molecules, and looking for the reduction of droplet size due to the evaporation and sublimation following from heat released as a result of heterogeneous nucleation of the solid phase.

APPARATUS AND MEASUREMENTS

The apparatus used here is the same as used previously [3]. A catalytic converter provided p-H$_2$. Freejets were formed via expansions from supercritical source conditions through a 5-µm-dia orifice. The central core of the freejet passed through a skimmer located 10mm from the orifice. The resulting droplet beam passed then through seven stages of pumping to a mass spectrometer with resolution adequate for mass spectra up to 360 amu. Capture of CO molecules by the beam droplets was facilitated by adding CO to the chopper chamber, located immediately downstream from the skimmer. The mean size, $\overline{N}$, of droplets leaving the scattering chamber was measured using

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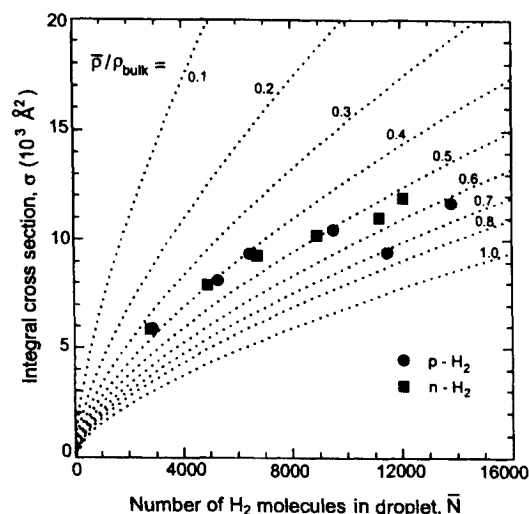
FIGURE 1. Integral cross sections deduced from attenuation of the droplet beam by a secondary beam as a function of droplet size. Classical integral cross sections for spheres with the indicated densities are shown as dotted lines.

small-angle scattering deflection by single collisions with an Ar secondary beam crossing the droplet beam at 40° [4].

As part of a preliminary characterization of the droplet beam, values of the H_2-droplet integral cross section were deduced from the attenuation of the droplet beam by the Ar secondary beam with no CO present in the scattering chamber [5]. These deduced values of the cross section are compared in Fig. 1 with classical integral cross sections calculated for spheres with several different values of average density. The effective droplet density implied by this comparison ranges from about 40% of the bulk density for $\overline{N}$ = 3,000 to about 60% of the bulk density for $\overline{N}$ = 14,000. Similar values for the effective density have been found for ^{4}He droplets, and the deviation from the bulk density was shown to be due to the density decrease near the surface [6]. No differences between p-H_2 and n-H_2 were noted.

Experimental arrangements were selected from three source gases (p-H_2, n-H_2 and ^{4}He), four average droplet sizes and two scattering-chamber arrangements. See Table 1. The selected source conditions all yield expansion paths which cross the binodal line on the gas-phase side of the critical point, so that the measured distribution of droplet sizes was log-normal, in agreement with measurements for ^{4}He [4].

For droplets containing initially about 5,000 H_2 molecules, the mean droplet size downstream from the scattering region was measured, again using small-angle scattering deflection [4], for several different values of the CO pressure, i.e., for several different values of the number of collisions in the scattering chamber. Possible contributions to the droplet size reductions include (a) evaporation as a result of energy transfer to the droplet in the collisions and (b) evaporation as a result of liquid-to-solid phase change should the capture of CO molecules lead to heterogeneous nucleation of solid H_2. The measured values of droplet size are shown as a function of CO pressure, alternatively number of collisions with CO molecules, in Fig. 2.

TABLE 1. Experimental arrangements. For experiments A and D – F, the scattering region is the chopper chamber with L = 90 mm and with the entrance at the skimmer whereas, for experiments B and C, the scattering region is the scattering chamber with L = 283 mm and with the entrance 422 mm from the skimmer. For experiment B, p_0 = 40 bar whereas, for all other experiments, p_0 = 20 bar. Most probable speed of CO molecules in the scattering region (300K) = 422 m/s.

Experiment	Beam Species	Droplet Size	Droplet Speed (m/s)	T_0 (K)
A	p-H_2	5,000	891	45
B	^{4}He	5,000	384	15
C	n-H_2	5,000	893	45
D	n-H_2	1,900	1024	55
E	n-H_2	13,700	790	40
F	n-H_2	5,600	887	45
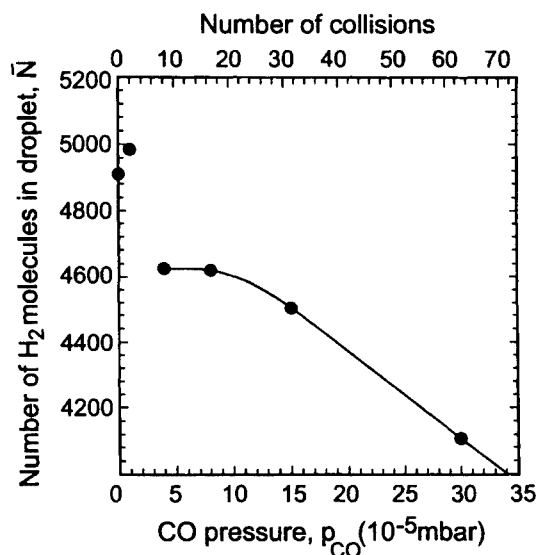
FIGURE 2. Average size of H_2 droplets after passing through CO scattering gas as a function of CO pressure (lower abscissa) or number of collisions (upper abscissa).

For each experimental arrangement, mass spectra were measured for several values of CO pressure in the scattering chamber. See Fig. 1 of Ref. 3. The peaks were found to be spaced at amu intervals slightly greater than 28, suggesting some hydrogen attachment to the CO clusters.

H_2 LOSSES INITIATED BY COLLISIONS

The average H_2 droplet size shown in Fig. 2 as a function of number of collisions experienced by the droplet in the scattering chamber is very descriptive of events in the life of the droplet. Consider the relatively dramatic loss of about 350 molecules sometime between the 2nd and the 8th collision. Since this loss appears to be a one-time event, and is several times larger than anticipated as a consequence of energy transfer to the droplet during collisions, an examination of the loss which would result from the heat which would be released if solid-phase nucleation were initiated by the captured CO molecules is motivated.

If the droplet solidifies, it is warmed by the heat of fusion and subsequently cooled by evaporation and sublimation. Experience shows that the number of H_2 molecules lost for a model of these processes is not very sensitive to the model details. Consider first the time required for heat diffusion within the droplet. A suitable characteristic time is provided by R^2/α, where R is droplet radius and α is thermal diffusivity. For the present purposes, use of the thermal diffusivity of the liquid at the triple point is satisfactory. Using this value, namely 1.4 x 10^{-3} cm^2/sec [7], one obtains for a droplet of 5000 molecules, for which R^2 is of the order of 2.6 x 10^{-13} cm^2, a characteristic time of 2 x 10^{-10} sec. This time is so short in comparison with other characteristic times of the experiment that one can consider the temperature within the droplet to be uniform. Hence a simplified three-step model with (1) constant-enthalpy partial solidification of the droplet as it warms to the triple-point temperature, (2) isothermal completion of the solidification with the heat of fusion going into evaporation, and (3) sublimation cooling of the solid droplet to either the characteristic temperature of sublimating droplets or some intermediate temperature if the cooling is interrupted by collisions was examined. Since a constant-enthalpy process does not require heat or mass exchange with the surroundings, the first step can be a very rapid step. As the droplet is warmed by the heat of fusion, the triple-point temperature is the first temperature reached at which the liquid and solid states can coexist in quasi-equilibrium.

The fraction solidified in the first step can be determined from

$$h_L(T_1) = fh_S(T_t) + (1-f)h_L(T_t)$$

where h is specific enthalpy, f is the fraction solidified, and the subscripts L, S, 1 and t refer respectively to liquid, solid, initial temperature and triple-point temperature. The fraction vaporized in the second step can be calculated from

$$x\Delta h_V + (1-f-x)\Delta h_F = 0$$

where x is the fraction vaporized, Δh_V is the enthalpy change for vaporization and Δh_F is the enthalpy change for fusion. The fraction of the remaining solid droplet which is lost via sublimation in the final step can be estimated from

$$h_S(T_t) = yh_V(\overline{T}) + (1-y)h_S(T_2)$$

where y is the fraction sublimated, $\overline{T}$ is to good approximation the average of the triple-point temperature and the final temperature, and the subscripts V and 2 refer respectively to vapor and final temperature. The enthalpy values are obtained either directly or by extrapolation from McCarty et al. [7]. On the basis of a separate analysis of the elevation of the droplet temperature due to multiple collisions of the beam droplets with CO molecules (Appendix A), the droplet temperature before and after the solidification was equated to 6K, about 2K higher than the temperature which would be reached ultimately as a result of evaporative cooling without collisions. Since the triple-point temperature is 13.8K, let $\overline{T}$ = 10K. Then one obtains f = 0.54, x = 0.053 and y = 0.020 so that the total fraction lost to evaporation and sublimation is z = x + y(1-x) = 0.072. Hence, for a droplet containing initially 5,000 H_2 molecules, 360 molecules would be lost. The agreement with the measured loss is taken to be evidence that the droplet was liquid prior to collisions with the CO scattering gas and that heterogeneous nucleation occurred sometime between the 2nd and the 8th collision.

The relatively small decrease in droplet size seen for the region of Fig. 2 between about 8 and 20 collisions is reminiscent of the initial small decrease in droplet size seen in Fig. 12 of Ref. 5 for ^{4}He droplets colliding with either Xe or SF_6. Probable bases for this relatively small decrease in droplet size include (a) the distortion of the droplet size distribution toward larger droplets due to preferential scattering of small droplets out of the beam, as indicated by Monte Carlo simulations [8], and (b) the lesser heat released when binding CO to the H_2 droplet, about 206K, than when binding CO to a pre-existing CO cluster within the H_2 droplet, about 727K.

For larger values of the CO pressure, a loss of about 25 H_2 molecules per collision was deduced from the reduction in droplet size with increase of CO pressure, i.e., from the straight-line portion of the curve in Fig. 2. As a check on this interpretation, this loss can be compared with that predicted for a model in which the energy transferred to the cluster as a result of a collision is equated to the energy required to evaporate ΔN H_2 molecules. For this model,

$$E_B[H_2 - (H_2)_N]\Delta N = (5/2)kT_{CO} + (1/2)m_{CO}v_{Cl}^2 + E_B[CO - (CO)_n]$$

where $E_B[H_2 - (H_2)_N]$ is the binding energy of an H_2 molecule to the liquid H_2 cluster, $(5/2)kT_{CO}$ is the sum of the rotational and random translational energies of the CO molecule, $(1/2)m_{CO}v_{Cl}^2$ is the kinetic energy of a CO molecule moving with speed v_{Cl} relative to the H_2 cluster and $E_B[CO - (CO)_n]$ is the binding energy of a CO molecule to the CO cluster. We use here the binding energy of a CO molecule to a CO cluster rather than the binding energy of a CO molecule to the H_2 droplet since we are examining the straight-line portion of the curve in Fig. 2, for which the number of collisions is greater than about 30 so that the size of the embedded CO cluster is sufficient to dominate the binding. For an H_2 binding energy of 107K, a CO temperature of 300K, a relative speed of 891 m/sec and a CO binding energy of 727K, one obtains ΔN = 26, which is considered to be in excellent agreement with the value deduced from the measurements.

Taking into account losses due to both collisions and solidification, we estimate that, for the droplet sizes occurring here, from 8 to 16 percent of the droplet mass was lost. Additional information regarding these losses of molecules is provided by an estimate of the fraction φ of molecules contained initially in the surface layer. For a very simplified model in which the density is uniform, purely geometrical considerations yield [9]

$$\varphi = 3v(1 - 0.5v)^{1/3}$$

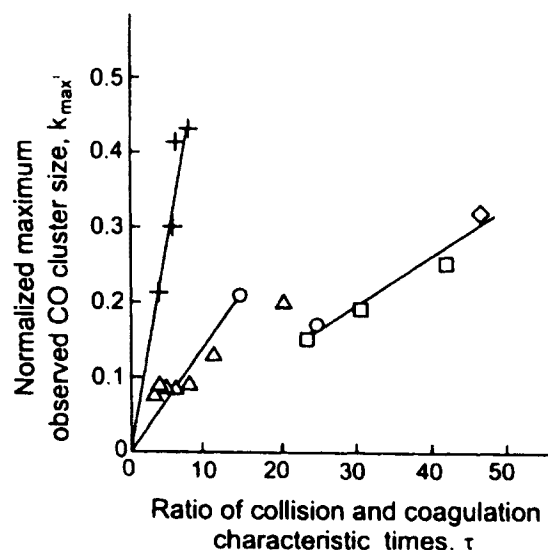where $$v = (4\pi/3N)^{1/3}$$

FIGURE 3. Normalized maximum observed CO cluster size k_{max}' as a function of the time between consecutive collisions divided by the characteristic time for coagulation. $\circ$ Experiment A, p-H_2. $+$ Experiment B, ^{4}He. $\square$ Experiment C, n-H_2. $\lozenge$ Experiment D, n-H_2. $\triangle$ Experiment E, n-H_2. The experiment arrangements are for three average droplet sizes and two scattering-chamber arrangements. See Table 1 for further details.

For $\bar{N}$ = 1,900, 5,000 and 13,700, one obtains φ = 0.34, 0.26 and 0.19 respectively. Hence the fraction lost due to both collisions and solidification is always less than the fraction contained in the surface layer of the droplet.

SIZE OF EMBEDDED CO CLUSTERS

As a measure of the efficacy of the capture and coagulation process, the maximum number k_{max} of CO molecules observed in the CO clusters was compared with the number of collisions with the CO gas via

$$k_{max}' = k_{max}/n_{CO}\sigma LF$$

where n_{CO} is the CO number density in the scattering region, σ is the integral cross section of the beam clusters, L is the length of the scattering region and F is a factor which takes into account the velocity distribution of the CO molecules in the scattering region [10]. The observed values for k_{max}' appear to depend on τ, the time between collisions of a beam droplet with the scattering-gas CO molecules divided by the characteristic time for coagulation, where the characteristic time for coagulation is simply the H_2-droplet volume divided by the diffusion-limited rate constant for coagulation of a CO molecule moving randomly inside an H_2 which already contains a CO cluster. Following Ref. 3, we model the rate constant by

$$k_D = (2/3)(kT/\mu)(1 + n^{1/3})^2/n^{1/3}$$

where k is Boltzmann's constant, μ is viscosity and n is the number of CO molecules in the CO cluster. This dependence is shown in Fig. 3. In agreement with conclusions reached by Lewerenz et al. [5], no correction was made for possible fragmentations of the CO clusters during detection. The value of the viscosity appearing in the rate constant, and hence in the characteristic time for coagulation, was based on the time-averaged droplet temperature calculated taking into account the temperature elevation due to multiple collisions of the beam droplets with CO molecules. Values for H_2 were obtained by extrapolating from values given by McCarty et al. [7], which required extrapolating from the triple point (13.8 in the case of p-H_2) to about 6K; values for ^{4}He were obtained by extrapolating from the values given by Woods and Hallett [11], which required extrapolating from 0.79K to about 0.55K. In the evaluation of the abscissa and ordinate, the loss in droplet size described in the previous section was not included. Taking it into account would increase the average value of the ordinate by about 4% and the average value of the abscissa by about 10%. This refinement would not alter the conclusions reached here.

Fig. 3 includes data for p-H_2, n-H_2 and ^{4}He droplets, for three average droplet sizes and for two scattering-chamber arrangements. See Table 1. The three straight lines, each passing through the origin, are drawn as guides to the eye. The difference in the slopes of the two straight lines drawn for the H_2 droplets is an indication of two significantly different capture and/or coagulation processes. The difference appears to be rooted in the frequency with which the H_2 droplet collides with the background CO molecules. Apparently, when the collision frequency exceeds some threshold value, the rate at which energy is transferred to the droplet via the collisions is sufficient to melt at least a portion of the droplet for at least some fraction of its time in the scattering chamber, with the result that both the capture cross section and coagulation rate are enhanced. A quantitative calculation of the rise and fall of the temperature of the droplet as it collides consecutively with scattering molecules would be formidable. However, the calculations of the droplet temperatures, averaged over the temperature peaks and valleys, do indeed indicate a higher average temperature for those droplets associated with the line having the higher slope.

It is anticipated that the capture coefficient for the ^{4}He droplets in Fig. 3 is nearly unity. Hence the difference in the slopes for H_2 versus ^{4}He is due apparently to a combination of reduced capture cross section and reduced coagulation rate for the H_2 droplets.

Fig. 3 contains data obtained using two different scattering regions, one with entrance at the skimmer and one with entrance 422 mm from the skimmer. When using the latter scattering region, no reduction in the size of the embedded CO clusters was observed, confirming the expectation that this increase in flight time for the droplets does not initiate homogeneous nucleation of the solid phase.

CONCLUSIONS

The agreement of (a) the predicted number of H_2 molecules lost due to evaporation/sublimation in the event of droplet solidification and (b) the measured number of H_2 molecules lost when CO molecules were captured by the droplets is taken to be evidence that the H_2 droplets were liquid prior to their collisions with the CO scattering gas. The observed dependence of the maximum CO cluster size on the collision frequency appears to indicate that a sufficiently high collision frequency will liquefy a droplet which otherwise would be solid. This compelling evidence in favor of a liquid state, coupled with the estimated 4K droplet temperature, suggest strongly that the supercooled H_2 droplets are superfluid. One of the most interesting results of this study is the indication that the capture of more one CO molecule is required to nucleate a phase transition to a solid. This opens up the possibility of seeking evidence of superfluidity by spectroscopic interrogation of probe molecules as shown for ^{4}He droplets [12].

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APPENDIX A. DROPLET HEATING DUE TO COLLISIONS

In the case of multiple collisions of the beam droplets with CO molecules in the scattering region, the droplet temperatures are elevated as a result of energy transfer to the droplets during the collisions. The temperature of an individual droplet increases during each collision and decreases due to evaporation during the time period between collisions; an average of these peaks and valleys approaches asymptotically a value which can be determined by equating (a) the product of the collision frequency and the energy transfer to the droplet per collision to (b) the product of the droplet surface area and the energy loss per unit area and per unit time due to the temperature-dependent evaporation process. The utility of using such an average of these peaks and valleys has been demonstrated by Hartmann et al. [13] in a study of the temperature elevation of ^{4}He droplets via collisions with a ^{4}He scattering gas. For the H_2 droplets, the energy transfer to the droplet per collision was deduced from the measured number of H_2 molecules lost per collision. One obtains the expression

$$n_{CO}\pi R^2 u_\infty \Delta N \Delta H_V = 4\pi R^2 \Delta H_V A[\exp(-\Delta H_V/kT]/(2\pi mkT)^{1/2}$$

where u_o is the mean speed of the beam droplets, $A\exp(-\Delta H_V/kT)$ is an approximate expression for the equilibrium vapor pressure of the bulk liquid and m is the mass of the H_2 molecule. (See Appendix B for a convenient expression for the vapor pressure of a droplet and a simple criterion for approximating the vapor pressure by that for the bulk liquid.) For droplets containing about 5,000 H_2 molecules and for experimental conditions such that about 26 H_2 molecules are lost per collision, the droplet temperatures at the exit of the scattering region were calculated to be about 6K, i.e., about 1K higher than at the end of the adiabatic expansion and about 2K higher than the temperature reached as a result of evaporative cooling in the absence of collisions. The relatively small size of the temperature rise is a consequence of the dominant factor $\exp(-\Delta H_V/kT)$ in the temperature dependence of the evaporation rate.

APPENDIX B. DROPLET VAPOR PRESSURE

The approximate expression for the vapor pressure used in Appendix A is that for the equilibrium vapor pressure of the bulk liquid. In principle, and as shown apparently first by Thompson [14], the equilibrium vapor pressure $p(R)$ of a liquid droplet of radius R is larger than equilibrium vapor pressure p_∞ of the bulk liquid according to

$$p(R)/p_\infty = \exp(2sv/RkT)$$

where s is surface tension and v is the droplet volume per molecule. The surface tension can be related to the heat of vaporization according to Eq. (11) of Ref. 15

$$sv^{2/3} = (1/6)\Delta H_V$$

Eliminating the surface tension from these two relations, one obtains

$$p(R)/p_\infty = \exp[(v^{1/3}/3R)(\Delta H_V/kT]$$

In Appendix A, the vapor pressure of the bulk liquid was written in the approximate form

$$p_\infty = A\exp(-\Delta H_V/kT)$$

so that the equilibrium vapor pressure for the liquid droplet may be written in the exceedingly convenient form

$$p(R) = A\exp[-(1-v^{1/3}/3R)\Delta H_V/kT]$$

This form suggests a very simple criterion for applicability of the expression for the bulk liquid for the case of liquid droplets, namely $v^{1/3}/3R \ll 1$. For a droplet containing 5,000 H_2 molecules, typical of those investigated here, $v^{1/3}/3R$ is approximately 0.02, so that the calculated temperature at the end of the flight path is only about 2% less than that calculated using the vapor pressure of the bulk liquid; the approximation made by the use of the vapor pressure for the bulk liquid is see to be justified.

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